

## C. Advanced Oxidation of PAN Fiber Precursor

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### Objectives

- Develop an improved technique for oxidizing carbon-fiber precursor with increased line speed, reduced carbon-fiber cost, and reduced equipment footprint.
- Verify that finished fiber properties satisfy automotive and heavy-vehicle manufacturers' requirements.
- Conduct a preliminary evaluation of the cost impact of the new oxidation technique.
- Integrate the oxidation module into an advanced-technology pilot-line.

### Approach

- Develop a plasma process for oxidation in an atmospheric-pressure plasma reactor.
- Develop fiber-handling protocols for continuous processing.
- Conduct parametric studies to correlate processing parameters and fiber properties.
- Characterize fibers to confirm that they satisfy program requirements.

### Accomplishments

- Demonstrated complete oxidation of "pre-stabilized" 3k PAN-precursor tow in atmospheric-pressure plasma using a continuous process at 0.05 m/min line speed.
- Fully oxidized "pre-stabilized" fiber in atmospheric-pressure plasma at less than half the residence time of conventional oxidation.
- Submitted a provisional patent application for the plasma oxidation process.

## **Future Direction**

- Continue refining the reactor design and processing protocols to achieve high speed, multiple large tow, continuous, plasma oxidation process.
- Develop “pre-stabilization” technique.
- Conduct parametric studies and fiber characterization to better understand process effects and the processing window and to quantify fiber properties.
- Conduct rate-effect studies and update cost analysis.

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## **Introduction**

The purpose of this project is to investigate and develop a plasma processing technique to rapidly and inexpensively oxidize a polyacrylonitrile (PAN) precursor. Oxidative stabilization is a slow thermal process that typically consumes 70% or more of the processing time in a conventional carbon-fiber conversion line. A rapid oxidation process could dramatically increase the conversion line throughput and appreciably lower the fiber cost. A related project has already demonstrated the potential for greatly increasing line speed in the carbonization and graphitization stages, but the oxidation time must be greatly reduced to fully exploit faster carbonization and graphitization. This project intends to develop a plasma oxidation module that integrates with other advanced fiber-processing modules to produce inexpensive carbon fiber with properties suitable for use by the automotive industry. Critical technical criteria include (1)  $\geq 25$  Msi tensile modulus and  $\geq 1.0\%$  ultimate strain in the finished fiber; (2) uniform properties over the length of the fiber tow; (3) repeatable and controllable processing; (4) and significant unit cost reduction compared with conventional processing.

## **Project Deliverable**

At the end of this project, we will have demonstrated satisfactory fiber oxidation in a multiple-tow, plasma oxidation module operating at line speed exceeding that typical of conventional carbon-fiber conversion lines.

## **Technical Approach**

We are investigating PAN-precursor-fiber oxidation using nonequilibrium, nonthermal plasma at atmospheric pressure. Plasma processing is believed to enhance oxygen diffusion and chemistry in the PAN oxidation process. Atmospheric-pressure

plasma provides better control over the thermal environment and reaction rates than does evacuated plasma, in addition to eliminating the sealing problems accompanying evacuated plasma processing. Various fiber characterization tools and instruments are used to conduct parametric studies and physical, mechanical, and morphological evaluations of the fibers to optimize the process. An evacuated plasma reactor is useful for bench-scale studies, because it allows a greater degree of manipulation and control over reactive species and related parameters. Early in the project, processing tests were conducted in an evacuated plasma reactor, and that same reactor is now used for conducting the bench-scale parametric studies.

## **Atmospheric-Pressure Plasma Processing Results**

Exposure in plasma at or near atmospheric pressure provides superior thermal control because the gas flow should convectively heat or cool the fibers. This is deemed particularly important to avoid fiber melting from the exothermic reactions associated with the PAN cross-linking that occurs during stabilization. However, the mean-free-path of the chemically reactive species is shorter by orders of magnitude than it is in an evacuated environment, and this makes it very difficult to find a combination of process parameters that will oxidize the fibers with acceptable residence time.

Conventional PAN oxidation is typically accomplished in three or four thermal stages (stages can be physically separate furnaces or zones in a single physical furnace) in air, at temperatures increasing from about 200 to 250°C. In FY 2004, the researchers demonstrated the ability to reproduce the oxidation advancement in each of the conventional furnaces two, three, and four. The virgin PAN is chemically fragile; hence, we have not yet

discovered a satisfactory nonthermal processing protocol that reproduces the oxidation advancement in the first conventional furnace. The researchers previously reported that they had been able to reproduce, with plasma oxidation, the process for each of the individual conventional furnaces 2, 3, and 4 (schematically shown in Fig 1).

During the first half of FY2005, the researchers refined the operating parameters to enable full oxidation of “pre-stabilized” precursor in a single step. i.e., the oxidation advancement achieved in a single, plasma, batch reactor was equivalent to that achieved in sequential processing through conventional furnaces 2, 3, and 4. This is shown schematically by the longest solid arrow in Figure 1. After batch oxidation was satisfactorily demonstrated, the researchers turned their attention to continuous processing. In the second half of FY2005, a continuous reactor was designed and built. The continuous- reactor design includes many innovations not present in earlier designs, but pictures and design details are not included herein due to the sensitive nature of that information. At the end of FY2005, the researchers demonstrated complete oxidation, starting with a “pre-stabilized” precursor, at a continuous processing line speed of 0.05 m/min.

Another very important achievement during this period was a significant reduction in oxidation residence time. The aforementioned single-stage, batch and continuous, plasma oxidation processes were achieved in less than half of the residence time required for conventional processing through furnaces 2, 3, and 4.

The researchers continued identifying the parameters that most affect the oxidation rate and optimizing those parameters within the reactor. For patent protection and export control reasons, the detailed results are not published, but they are periodically disclosed to the relevant program managers in oral briefings.

### **Pre-Stabilization**

As previously mentioned, the precursor must be lightly stabilized before it can withstand the plasma environment. Late in FY2005, a new project was initiated to focus on developing an advanced “pre-

stabilization” technique (See report 3.B, “Advanced Stabilization of Pan Fiber Precursors”). The pre-stabilization module and the plasma oxidation module will eventually be incorporated into an advanced-technology pilot-line.

### **Future Direction**

In FY 2006, the project focus will be on carbonizing plasma-oxidized fiber to validate its mechanical properties; parametric studies to improve the process; and commence scaling studies to increase line speed, tow size, and tow count.

### **Patents and Publications**

A provisional patent application was filed describing the plasma oxidation method.

### **Education**

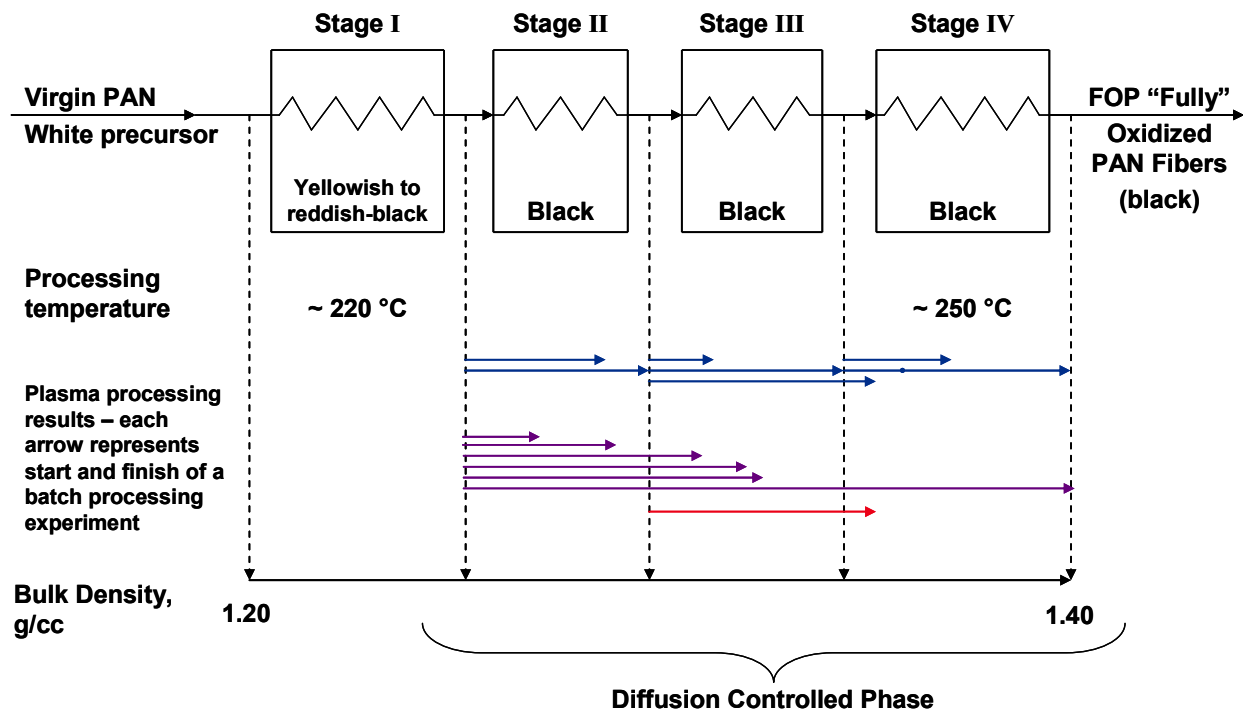
The materials characterization has been conducted in partnership with the University of Tennessee’s (UT’s) materials science department. Two UT graduate students were engaged to provide characterization support to the project.

### **Partners**

ORNL gratefully acknowledges contributions to this project by Fortafil and Hexcel. Both have generously provided raw materials and offered technical consultation. Additionally, technical and programmatic consultation has been provided by the Automotive Composites Consortium and by Delphi Corporation.

### **Conclusions**

During FY 2005, the researchers have fully oxidized “pre-stabilized” PAN in a single-step, batch process and in a continuous process, in less than half of the residence time required for analogous conventional thermal processing. The next steps are to validate mechanical properties and commence scaling studies.



**Figure 1.** Oxidation advancement—arrows show degree of advancement achieved in various batch plasma processing experiments. Different arrow patterns represent different schemes.